

Production of surfaces to which liquids do not adhere

The present invention relates to a process for producing surfaces  
5 to which, at a temperature  $T \geq T_1$ , liquids A do not adhere or  
adhere only poorly, and in particular for producing surfaces with  
low susceptibility to soiling. The invention also relates to  
articles which have at least one such surface.

- 10 Conventional surfaces are generally wetted by liquids. The degree  
of wetting depends on interplay between the cohesion forces  
within the liquid and the adhesion forces between liquid and  
surface. The contact angle of a liquid droplet on a surface is  
frequently utilized as a measure of the wettability of that  
15 surface by the liquid (see Barthlott et al., *Biologie in unserer  
Zeit*, 28, No. 5, 314-322; K. Henning, *SÖFW-Journal, Chemische  
Spezialitäten* 127 (2001), pp. 96-107). Another measure of the  
adhesion of a liquid on a surface, i.e. the adhesion of liquid  
droplets on a surface, is the contact angle hysteresis. The  
20 contact angle hysteresis  $\Delta\theta = \theta_a - \theta_r$  is the difference between the  
advancing contact angle  $\theta_a$  and the receding contact angle  $\theta_r$  for a  
liquid droplet running off a surface (Dörfler in *Grenzflächen und  
kolloiddisperse Systeme*, Springer-Verlag Berlin Heidelberg New  
York 2002, pp. 85-88). The greater the contact angle hysteresis,  
25 the stronger the adhesion of the liquid droplet to the surface,  
and the smaller the running-off tendency of liquid droplets on  
inclined surfaces. The same applies to the wettability of the  
surface by a liquid.
- 30 The prior art defines the contact angle  $\theta$  as the angle enclosed by  
said surface and a tangent along the surface of the liquid  
droplet in the region of the location of contact of the liquid  
droplet with the surface, the contact angle being measured  
through the liquid droplet. The advancing contact angle  $\theta_a$  is the  
35 contact angle of the droplet on the side in the direction of  
movement, and the receding contact angle  $\theta_r$  is the contact angle  
on the side opposite to the direction of movement. The static  
contact angle for a droplet at rest is a different parameter (see  
Dörfler, loc. cit. Sections 4.7 and 4.8, pp. 87 et seq.).  
40 The soiling of surfaces is a general occurrence in everyday life,  
both in households and in industry. Laborious cleaning work is  
needed to remove stains or dirt. A typical example is provided by

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ring-shaped stains produced during drying-out of water or aqueous solutions, e.g. stains resulting from hard water, raindrops, and the like. Stains resulting from coffee, tea, juices, or red wine are particularly problematic. Other examples of undesirable dirt are provided by soot, dust, spores, pollen, and bacteria. These contaminants are not only unsightly but can also cause degradation of coatings and surfaces and result in hygiene problems, particularly in hospitals, abattoirs, and sanitary installations.

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The soiling of surfaces is closely related to the wettability of the surface by liquids (see Barthlott et al., *Biologie in unserer Zeit*, 28, No. 5, 314-322; K. Henning, *SÖFW-Journal*, 127 (2001), pp. 96-107) and the adhesion of liquid droplets to a surface. For example, a result of the wetting of surfaces with water is that water droplets remain on the surface and evaporate, whereupon the solids dissolved or suspended in water remain on the surface as undesirable residues. This problem is particularly in evidence with surfaces exposed to rainwater. The wetting of a surface with water also frequently initiates its corrosion or infestation with microorganisms, or else its colonization by algae, lichens, mosses, bivalves, etc. This in turn results in biocorrosion of the surface.

It is also known that dirt particles on rough, hydrophobic surfaces are washed away from the surface by moving water (see Barthlott et al., loc. cit. and WO 96/04123). This effect stems from the low adhesion of the water droplets on the rough, hydrophobic surfaces, and is also termed the self-cleaning effect or Lotus effect.

EP-A 933 388 discloses a process for producing structured surfaces with hydrophobic properties, by firstly producing a negative mold by photolithography, using this mold to emboss a plastic film, and then hydrophobicizing the plastic film with fluoroalkylsilanes.

EP-A 909 747 describes a process for generating self-cleaning properties on ceramics, such as roof tiles, by applying a dispersion of clay particles in an organic silicone resin solution to the ceramic and curing the coating.

The methods described in the prior art for producing low-wettability surfaces are generally very complicated and frequently do not give satisfactory results. Another disadvantage of the known low-wettability surfaces is their susceptibility to surfactant-containing liquids and oil- or fat-containing

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contaminants. The known low-wettability surfaces frequently have an unsightly matt appearance.

It is an object of the present invention, therefore, to provide  
5 another process for producing surfaces to which liquids have low adhesion. The process should permit the controlled production of the surfaces of this type to which liquids other than water exhibit low adhesion. The process should also be simple to carry out and should minimize the disadvantageous effect on the  
10 appearance of the surfaces.

We have found that this object is achieved, surprisingly, by means of a process in which a substance B which is immiscible with the liquid A or soluble therein to an extent of less than  
15 0.1 g/l (at 20°C and 1013 mbar) and has been selected from low-molecular-weight, oligomeric, or polymeric liquids is applied to a surface S present on a substrate or an article and having many depressions and/or elevations, the average distance between adjacent elevations being in the range from 0.01 to 500 µm, and  
20 the average height difference between mutually adjacent elevations and depressions is in the range from 0.01 to 500 µm, where the amount applied covers the surface.

The term liquid used here means substances B which, at the lowest  
25 desired usage temperature T<sub>1</sub>, remain liquid or, in the case of polymeric liquids, have no flow threshold. The flow threshold is defined as the minimum shear stress above which a plastic material has the rheological behavior of a liquid. A plastic material which has no measurable flow threshold therefore has the  
30 rheological behavior of a liquid even when no measurable shear stress is applied. The external forces required for its flow are therefore zero or only tiny (see Römpp-Lexikon, Lacke und Druckfarben, Georg-Thieme-Verlag 1998, Stuttgart, p. 239).

35 The present invention therefore provides a process for producing articles or substrates with at least one surface on which a liquid A has low adhesion at a temperature  $T \geq T_1$ , by applying a substance B in liquid or in dissolved form to a surface S of the substrate or article in an amount which covers the surface S,  
40 which comprises using a surface S which has many depressions and elevations, where the average distance between adjacent elevations is in the range from 0.01 to 500 µm and the average height difference between mutually adjacent elevations and depressions is in the range from 0.01 to 500 µm, the substance B  
45 is immiscible with the liquid A and soluble therein to an extent of less than 0.1 g/l (at 20°C and 1013 mbar), and has been selected from low-molecular-weight and oligomeric substances B<sub>1</sub>

which are liquid at the temperature T1 and polymeric liquids, i.e. plastic polymeric substances B2 which do not have a measurable flow threshold.

- 5 The terms advancing contact angle, receding contact angle, static contact angle and contact angle hysteresis are used here and below in accordance with the definitions which were mentioned at the outset and are conventional in the prior art. The contact angle is determined by methods known per se, for example with the aid of a microscope equipped with a goniometer (see Dörfler, loc. cit., pp. 75 et seq., and C. D. Bain et al., Angew. Chem. 101 (1989) 522-528, and A. Born et al., Farbe & Lack 105 (1999) pp. 96-104).
- 10
- 15 The nature of the substance B depends on the liquid A and on the nature of the surface for which low wettability is to be achieved. Firstly, the substance B has to be immiscible with the liquid A or soluble therein to an extent of less than 0.1 g/l, preferably less than 0.05 g/l, and in particular less than 0.01 g/l (at 20°C and 1013 mbar).
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Preference is given here to those substances B which, at  $T \geq T_1$ , have a static contact angle  $\theta_B < 10^\circ$  (e.g. at 20°C) on the surface, or have no measurable contact angle. This makes coating of the substrate surface easier.

25

It is self-evident that the substance B should have only low volatility at the usage temperature, in order to ensure durability of the coating. In particular, the vapor pressure of the substance B at the usage temperature, and as a minimum requirement at 20°C, should not exceed 0.1 mbar, in particular 0.01 mbar, or the boiling point of the substance B at atmospheric pressure should not be less than 200°C, in particular should not be less than 250°C.

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35 If the substance B is a polymeric substance B2, according to the invention the minimum requirement is that at the temperature T1 the substance has no measurable flow threshold, i.e. the substance B2 is capable of undergoing plastic deformation, and is therefore flowable, when subjected to no, or only tiny, shear stresses. This is generally the case when the polymeric substance B2 has substantially no crosslinking and has no crystalline domains.

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45 The lower limit of the usage temperature T1, above which there is a marked reduction in the adhesion of the liquid A, depends substantially only on whether at that temperature the substance B

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is liquid or has no flow threshold. The upper limit of the temperature, at which no, or only slight, wetting takes place depends only on the stability of the coating. In principle, therefore possible usage temperatures are in the range from -60 to 250°C, in particular in the range from -20 to 200°C, and specifically in the range from -10 to 150°C. Correspondingly, the value for T<sub>1</sub> used as a basis for selecting suitable substances B will frequently be a temperature  $\geq -60^{\circ}\text{C}$ , in particular  $\geq -20^{\circ}\text{C}$ , and specifically  $\geq -10^{\circ}\text{C}$ . Low wettability is frequently desired at temperatures  $\geq -10^{\circ}\text{C}$ , e.g. from -10 to 100°C, and in particular from 0 to 50°C. In this case, this value for T<sub>1</sub> will be used as a basis for selecting the substance B. One preferred embodiment of the invention therefore provides a process which uses a substance B which is liquid at -10°C and in particular, as a minimum requirement, at 0°C, or as an alternative has no flow threshold at -10°C or, respectively, 0°C and above. If the polymeric substance has a glass transition, the associated glass transition temperature is preferably below T<sub>1</sub> by at least 5 K, in particular at least 10 K, and specifically by 20 K. Preference is therefore given here to those substances B<sub>2</sub> whose glass transition temperature is  $\leq -5^{\circ}\text{C}$ , in particular  $\leq -10^{\circ}\text{C}$ , and specifically  $\leq -20^{\circ}\text{C}$ .

If the low wettability is desired only at relatively high temperatures, e.g.  $\geq 50^{\circ}\text{C}$ , this temperature T<sub>1</sub> will be used as a basis for selecting suitable substances. One embodiment of the invention therefore provides a process for which T is  $\geq 50^{\circ}\text{C}$ , and the substance B has the required properties at 50°C and above.

With regard to the desired effect of low adhesion of the liquid A to the surface obtained according to the invention, the selection of the substance B is preferably such that it complies with the relationship of formula I

$$\gamma_B \cdot \cos(\theta_B) - \gamma_A \cdot \cos(\theta_A) - \gamma_{A/B} > 0 \quad (\text{I})$$

where

$\gamma_A$  is the surface tension of the liquid A  
 $\theta_A$  is the static contact angle of the liquid A on the untreated surface S  
 $\gamma_B$  is the surface tension of the substance B  
 $\theta_B$  is the static contact angle of the liquid substance B on the untreated surface S, and  
 $\gamma_{A/B}$  is the surface tension at the boundary between liquid A and substance B.

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The terms surface tension at the boundary, surface tension, and static contact angle in formula I have the conventional prior-art meaning (see, for example, Dörfel, loc. cit., Römpp, Chemielexikon, 10th Edition, pp. 1608 and 2975 et seq.) and

- 5 relate to the values applying at the temperature  $T_1$ . If  $T_1 \geq -10^\circ\text{C}$  and in particular  $\geq 0^\circ\text{C}$ ,  $\gamma_A$ ,  $\gamma_B$ ,  $\theta_A$ ,  $\theta_B$ , and  $\gamma_{A/B}$  may be based on the values applicable under standard conditions ( $25^\circ\text{C}$  and 1013 mbar). The values for  $\gamma_A$ ,  $\gamma_B$ , and  $\gamma_{A/B}$  may frequently be taken from the literature, e.g. from commercial databases, such as Winspircs  
10 Version 4.01, Silver Platter Software©, Silver Platter Ltd. N.V. 1999, and relevant manuals.

The surface tension  $\gamma_A$  of the liquid A and the surface tension  $\gamma_B$  of the substance B may be determined in a manner known per se,

- 15 e.g. by (a) formation of meniscus and height of rise in capillaries, (b) pressure of a gas bubble emerging into a liquid, (c) the ring method, (d) the Wilhelmy method, or (e) the method using the shape of supported or unsupported droplets (see, for example, Kohlrausch, Praktische Physik 1, pp. 200 et seq.,  
20 Stuttgart, Teubner 1996; for the unsupported drop (pendant drop) method see also S. Wu, "Polymer Interface and Adhesion", Marcel Dekker Inc., New York 1982, pp. 266-268). Values for the surface tension of liquids A are found by way of example in Handbook of Chemistry and Physics 76th Edition, CRC Press 1995, from 6-155 to  
25 6-158. Similarly, the surface tension at the boundary between liquid A and substance B can be determined by (a) weighing methods which measure the force which has to be exerted to draw a sheet or hoop out of a liquid, (b) droplet volume methods, (c) the "spinning drop" method, (d) bubble pressure methods, and (e)  
30 the pendant drop method (see, for example, Kohlrausch, Praktische Physik 1, pp. 230 et seq., Stuttgart, Teubner 1985). The surface tension of some commercially available polymers B2 is given in the literature; see, for example, S. Wu et al. loc. cit. pp. 88 et seq., and S. Ellefson et al. J. Am. Ceram. Soc. 21, 193,  
35 (1938); S. Wu, J. Colloid Interface Sci. 31, 153 (1969), J. Phys. Chem. 74, 632 (1970), J. Polym. Sci., C34, 19, (1971); R.J. Roe et al., J. Phys. Chem. 72, 2013 (1968), J. Phys. Chem. 71, 4190 (1967), J. Colloid Interface Sci. 31, 228 (1969); J.F. Padday in Surface and Colloid Science (Editor E. Matijevic), Wiley, New  
40 York 1969, pp. 101-149.

The surface tension at the boundary of substance B is preferably  $\leq 50$  mN/m, in particular is in the range from 5 to 45 mN/m, and specifically is in the range from 10 to 40 mN/m at  $20^\circ\text{C}$ , in

- 45 particular when the liquid A is an aqueous liquid.

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Examples of suitable substances B1 are

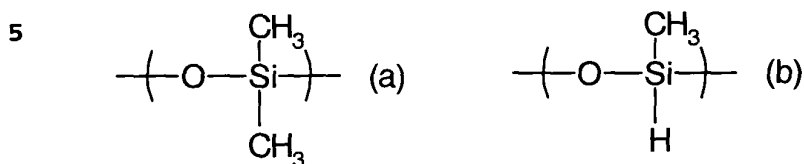
- low-molecular-weight hydrocarbons, in particular saturated hydrocarbons having at least 8 carbon atoms, preferably at least 10 carbon atoms, in particular from 10 to 20 carbon atoms, e.g. octanes, nonanes, decanes, decalin, undecanes, dodecanes, tetradecanes, hexadecane, and mixtures of these;
- perfluorohydrocarbons having at least 8 carbon atoms, preferably at least 10 carbon atoms, in particular from 10 to 40 carbon atoms, e.g. perfluorodecalins, perfluoroeicosanes, and perfluorotetracosanes, and mixtures of these; and
- alkanols having at least 8 carbon atoms, preferably at least 10 carbon atoms, e.g. 3-octanol, 1-decanol, 2-decanol, undecanols, dodecanols, tridecanols, 2-hexadecanol, 2-hexyldecanol, and mixtures of these.

Particular other suitable substances B are polyisobutenes, which, depending on molecular weight, may be liquids, high-viscosity liquids, or solids. These generally have a number-average molecular weight in the range from 300 to  $5 \times 10^6$  dalton, in particular in the range from 600 to  $3 \times 10^6$  dalton.

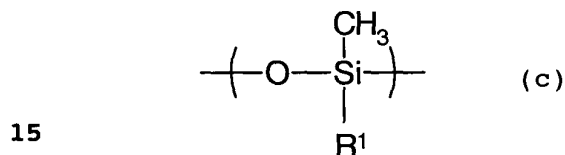
Other particular suitable substances B are silicones, which, depending on molecular weight, may be liquids, high-viscosity liquids, or solids. These generally have a number-average molecular weight in the range from 200 to  $10^6$  dalton, in particular in the range from 400 to  $3 \times 10^5$  dalton. The silicones are generally linear, branched, or cyclic polydimethylsiloxanes, or polymethylhydrosiloxanes. These may have the following groups G as end-groups or as side-chains: hydrogen, hydroxy groups, amino groups,  $C_1$ - $C_{20}$ -alkyl groups,  $C_1$ - $C_{20}$ -alkoxy groups, hydroxy- $C_2$ - $C_4$ -alkyl groups, formyl groups and  $C_1$ - $C_{20}$ -alkylcarbonyl groups, carboxy- $C_1$ - $C_{20}$ -alkyl groups, amino- $C_1$ - $C_{20}$ -alkyl groups, amino groups, N-(2-amino- $C_1$ - $C_4$ -alkyl)amino- $C_1$ - $C_{20}$ -alkyl groups, glycidyl or glycidyloxy groups, methylpolyoxyethylenealkyl groups, hydroxypolyoxyethylenealkyl groups, methylpolyoxyethylenepolyoxypropylene groups, hydroxypolyoxyethylene groups, polyoxyethylene groups, phenyl groups, or perfluoro- $C_1$ - $C_{20}$ -alkyl groups. Examples of preferred groups G, besides hydrogen, are  $C_1$ - $C_4$ -alkyl such as methyl or ethyl, OH, aminoalkyl, such as  $(CH_2)_{1-10}NH_2$ , methylpolyoxyethylenealkyl groups, such as  $(CH_2)_3-(OCH_2CH_2)_{1-10}-OCH_3$ , hydroxypolyoxyethylenealkyl groups, such as  $(CH_2)_3-(OCH_2CH_2)_{1-10}-OH$ , and amino groups, such as  $N(CH_3)_2$ .

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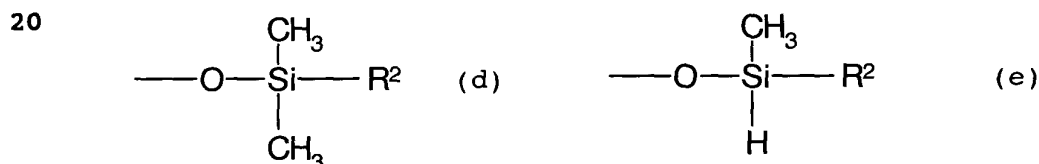
Polydimethylsiloxanes are generally composed predominantly of repeat units of the formula a, and polymethylhydrosiloxanes are generally mainly composed of repeat units of the formula b:



10 Where appropriate, they have one or more groups of the formula c:



and end-groups of the formulae d and/or e:



25  $\text{R}^1$  here is one of the abovementioned groups G other than hydrogen and methyl.  $\text{R}^2$  is as defined for G.

30 The polydimethylsiloxanes, and also the polymethylhydrosiloxanes, may be linear or branched, or cyclic, preference being given to linear polydimethylsiloxanes and polymethylhydrosiloxanes. If the groups of the formula (c) are present, their arrangement in the siloxane chain may be random or in blocks.

35 Examples of suitable silicones are:

- 40 - polydimethylsiloxanes with a molar mass of from 100 to 1000000 g/mol, preferably from 300 to 500000 g/mol, particularly preferably from 1000 to 200000 g/mol (number average);
- 45 - polymethylhydrosiloxanes with a molar mass of from 200 to 1000000 g/mol, preferably from 400 to 400000 g/mol, particularly preferably from 800 to 150000 g/mol (number average);



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- hydrogen-terminated polydimethylsiloxanes with a molar mass of from 100 to 900000 g/mol, preferably from 400 to 500000 g/mol, particularly preferably from 500 to 200000 g/mol (number average);

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- silanol-terminated polydimethylsiloxanes with a molar mass of from 200 to 800000 g/mol, preferably from 400 to 500000 g/mol, particularly preferably from 500 to 300000 g/mol (number average);

10

- amino-C<sub>1</sub>-C<sub>10</sub>-alkyl-terminated polydimethylsiloxanes with a molar mass of from 200 to 600000 g/mol, preferably from 300 to 400000 g/mol, particularly preferably from 400 to 300000 g/mol (number average);

15

- hydroxy-C<sub>1</sub>-C<sub>10</sub>-alkyl-terminated polydimethylsiloxanes with a molar mass of from 100 to 500000 g/mol, preferably from 150 to 300000 g/mol, particularly preferably from 180 to 200000 g/mol (number average); and

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- glycidyoxy-terminated polydimethylsiloxanes with a molar mass of from 150 to 400000 g/mol, preferably from 180 to 200000 g/mol, particularly preferably from 200 to 250000 g/mol (number average).

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Silicones of this type are known, e.g. from Moretto et al., Silicones, Chapter 3, in Ullmanns Encyclopedia of Industrial Chemistry, 5th edn. on CD-ROM, and are commercially available, for example with the trade name Rhodorsil (Rhodia) and from

30 Gelest ABCR, Tullytown, PA, USA.

Examples of other suitable substances B2 are:

- poly(alkyl acrylates) and poly(alkyl methacrylates), and  
35 copolymers of alkyl acrylates and alkyl methacrylates, as long as these are liquid or have no flow threshold. Examples of these are polymethyl acrylate, poly(n-propyl acrylate), poly(isobutyl acrylate), poly(n-butyl acrylate), poly(tert-butyl acrylate), polymethyl methacrylate,  
40 poly(n-propyl methacrylate), poly(isobutyl methacrylates), poly(n-butyl methacrylate), poly(tert-butyl methacrylate);
- polyesters preferably, such as poly(bisphenol A)  
terephthalate, poly(ethylene adipate), poly(ethylene  
45 terephthalate), poly(oxyethyleneoxyterephthaloyl),

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poly(oxy-pentamethyleneoxyterephthaloyl),  
poly(oxy-tetramethyleneoxyadipoyl).

The polymeric substances are suitable as long as at T<sub>1</sub> they are  
5 liquid or have no flow threshold at T<sub>1</sub>.

The nature and structure of the surface are of lesser importance  
as long as the surface has many depressions and/or elevations and  
the average distance between adjacent elevations is in the range  
10 from 0.01 to 500  $\mu\text{m}$ , in particular in the range from 0.05 to 200  
 $\mu\text{m}$ , particularly preferably in the range from 0.1 to 100  $\mu\text{m}$ , very  
particularly preferably from 0.2 to 80  $\mu\text{m}$ , and specifically from  
0.5 to 50  $\mu\text{m}$ . The average height difference between mutually  
adjacent elevations and depressions is preferably in the range  
15 from 0.05 to 200  $\mu\text{m}$ , and particularly preferably in the range  
from 0.1 to 100  $\mu\text{m}$ , very particularly preferably from 0.2 to 80  
 $\mu\text{m}$ , and specifically from 0.5 to 50  $\mu\text{m}$ . This ensures uniform  
adhesion of the substance B on the substrate surface. In so far  
as the structure of the surface is substantially composed of  
20 depressions in a base surface or of elevations on a base surface,  
the ranges of values given above apply to the average heights  
(maxima) of the elevations above the base surface and,  
respectively, to the average depths (minima) of the depressions  
in the base surface.

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The elevations/depressions may have a regular or irregular  
arrangement or may be of fractal character. Other suitable  
surface structures are those with irregularly arranged  
substructures which in turn have a regular arrangement. Examples  
30 of regular arrangements are waffle-pattern structures (isolated  
depressions in a flat surface), mountain-and-valley structures  
(= isolated elevations and isolated depressions, between which  
there are saddle areas, pillars and spikes (isolated elevations,  
e.g. pyramidal, block-shaped, irregular, or cylindrical, on a  
35 flat base structure), and stripes (= ribbon-shaped elevations on  
a flat surface, or linear depressions in a flat surface). Surface  
structures of this type are known and are described by way of  
example by Marzolin et al., Advanced Materials 1998, 10, pp.  
571-574, Thin Solid Film 315, 1998, pp. 9-12. Examples of  
40 surfaces with irregularly arranged elevations/depressions are  
structures obtained, for example, by fixing particulate materials  
to surfaces which are per se flat. Fractal surface structures and  
their production are described by way of example by Shibuichi et  
al., J. Phys. Chem. 1996, pp. 19512-19517. Examples of surfaces  
45 with irregularly arranged substructures which in turn have a

regular arrangement of elevations and depressions are the etched patterns obtainable when surfaces are etched.

- The elevations/depressions may also have a fine structure, i.e.
- 5 the elevations and depressions in turn have a number of elevations and/or depressions, and the distances and height differences between adjacent elevations/depressions of the fine structure are smaller by a factor of at least 5 than those of the associated main structures or overlying structures. The average
- 10 distance/height difference in the fine structures may be in the range from 5 nm to 1000 nm, and in particular in the range from 10 nm to 500 nm, depending on the size of the overlying structure.
- 15 The production of surfaces which have many depressions and elevations is known per se. By way of example, the production of surfaces with a regular arrangement of elevations and depressions is possible by photolithographic processes, as described by way of example in US 3,354,022, T. Ito et al., Jpn. J. Appl. Phys. 32
- 20 (1993) 6052, by embossing processes as described by Marzolin et al. (loc. cit.), Wilbur et al., Adv. Mater. 7, 1995, p. 649, Y. Xia et al., Langmuir 1996, 12, p. 4033, M. Toki et al., J. Non Cryst. Solids, 1988, 100, p. 479, a sol-gel process being used where appropriate here to form the structures, or by combining
- 25 photolithographic and embossing processes as described in EP-A 933 388 and by Marzolin et al. (loc. cit.). Substrates with surfaces which have many regularly arranged depressions and elevations in the size range given are also commercially available, e.g. as Truegrain® from Autotype International Ltd.,
- 30 Wantage, Oxon., United Kingdom.

- Surfaces with an irregular arrangement of elevations and depressions are a preferred embodiment of the invention, and can be produced in a particularly simple manner by applying a finely
- 35 divided particulate material of suitable size to a surface of an article, the surface being smooth per se, and fixing the material to the surface. Preference is given here to those particulate materials, also termed powders below, in which the particle sizes of 90% by weight of the particles are in the range from 0.01 to
- 40 500  $\mu\text{m}$ , in particular in the range from 0.05 to 200  $\mu\text{m}$ , particularly preferably in the range from 0.1 to 100  $\mu\text{m}$ , very particularly preferably in the range from 0.2 to 80  $\mu\text{m}$ , and specifically from 0.5 to 50  $\mu\text{m}$ . The powder may be inorganic or organic in nature. The powder particles may have a regular
- 45 structure, e.g. a spherical or ellipsoidal structure, or may have an irregular structure, e.g. a fractal structure, or a porous structure, or a structure formed by agglomeration. Examples of

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suitable particulate materials are organic powders, e.g. polymer powder, such as polyethylene powder, polypropylene powder, polytetrafluoroethylene powder, and bioorganic powders, such as lycopodium, and also inorganic powders, such as those based on  
5 silicon dioxide or on silicates, for example silica powder, e.g. precipitated silica, diatomaceous earth, fumed silica, porosils, and silica gel powder, clay minerals, powdered quartz, powdered glass, e.g. glass beads, and aluminum oxide, zeolites, and titanium dioxide, and oxidic powders here may also have been  
10 hydrophobicized with fluorinated organic silanes.

The amount of the powder applied is generally sufficient to give complete, at least 95%, covering of the surface by the powder particles.

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The powder particles may be fixed in any desired manner, which is of relatively little importance for the success of the process of the invention. For example, a surface may be provided with a pressure-sensitive adhesive. The powder is then usually applied  
20 by scattering. The excess powder, i.e. the powder not fixed, is then shaken off or blown off using a stream of air. Instead of the pressure-sensitive adhesive, use may also be made of a photo-crosslinkable adhesive or of a curable coating material, e.g. a photo-crosslinkable or hot-curing coating material. The  
25 powder is then applied in the manner described above, and is fixed by curing the adhesive or layer of coating material, e.g. by UV radiation. Any desired materials may be used as carriers for the powder particles or for the adhesives, examples being plastic films, metal, coated metal, ceramics, paper, leather,  
30 wood, and also fibers and yarns, and also construction materials, such as masonry, concrete, tiles, plaster surfaces, and the like.

The desired surfaces may also be obtained by chemical etching methods, e.g. by etching with acid or with a solvent, or by  
35 physico-chemical etching methods, e.g. using plasma radiation, ion etching in the presence of oxygen, or the like.

The character of the article or substrate possessing the surface, also termed substrate material below, is of relatively little  
40 importance for the success of the invention. Under the usage conditions, i.e. in the temperature range  $[T_1; T_2]$  within which low wettability is desired, the substrate material is naturally solid and gives a stable level of roughness, i.e. at temperatures above  $T_1$  it is unlike the polymeric substance B2 in having a high  
45 flow threshold or being incapable of plastic deformation. It has

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preferably been matched to the substance B in such a way that the contact angle on the given roughness is  $< 10^\circ$ .

- The substrate may be composed uniformly of one material, i.e.
- 5 elevations/depressions and any surface areas present between these are composed of one material. However, the substrate may also be composed of two or more materials. This is frequently the case when the substrate has been produced by applying particulate substances to a carrier. The substrate is then composed of the
- 10 carrier material, the particles which form the elevations/depressions, and, where appropriate, any means used to fix the particles to the carrier. The properties of the surface are generally unaffected by the carrier.
- 15 Examples of substrate materials are metals, such as iron, iron-containing alloys, e.g. steels, conventional coated surfaces, semimetals, such as silicon, and ceramic materials, plastics, e.g. polyolefins, such as polyethylene and polypropylene, polyesters, such as polyethylene terephthalate,
- 20 polyvinyl chloride, polystyrene, polyalkyl methacrylates, diene rubbers, EPDM rubbers, ABS, polyarylene ethers, polyether sulfones, polyurethanes, polyamides, polyacrylonitrile, styrene-acrylonitrile, polycondensation resins, and in particular crosslinked siloxanes, for example those produced during
- 25 condensation of organosilanols, and also blends of the abovementioned plastics, and composites of plastics with inorganic fillers.

- The substance B may be applied in a conventional manner to the
- 30 surface of the article, for example by dipping, spraying, rolling, spin-coating, frictional application, or migration, utilizing the capillary forces exerted by the surface. The last method is one preferred embodiment of the invention, and is in particular preferred for applying liquid substances B1.

- 35 When applied to the surface, the substance B is generally in liquid form or in dissolved form. If the substance B has been selected from liquids B1, it preferably has a viscosity  $\leq 10000$  mm<sup>2</sup>/sec and in particular  $\leq 5000$  mm<sup>2</sup>/sec, e.g. in the range from 5
- 40 to 10000 mm<sup>2</sup>/sec (at 20°C). The viscosity given here is the kinematic viscosity, for example as can be determined using an Ubbelohde viscometer to DIN 51562-1 to 4. Uniform application of the substance B becomes easier when the viscosity is within that range.

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If the substance B has a higher viscosity, or indeed is solid, it is advisable to dilute the substance B with a solvent or to dissolve it therein. This applies in particular when the substance B has been selected from polymeric substances B2. In this case, B2 is in the form of a solution in a low-molecular-weight solvent when applied to the surface. The viscosity of the solution here is preferably adjusted to values  $\leq 10000 \text{ mm}^2/\text{sec}$  and in particular  $\leq 5000 \text{ mm}^2/\text{sec}$ , e.g. in the range from 5 to  $10000 \text{ mm}^2/\text{sec}$  (at  $20^\circ\text{C}$ ). The selection of the solvent is of relatively little importance for the success of the process of the invention, and mainly depends on the substance B, for which it should be a good solvent. In addition, the solvent should cause no breakdown of the surface structure, and should be sufficiently volatile to be easily removable. The skilled worker will be able to find suitable solvents, using simple trials. Examples of suitable solvents are hydrocarbons, such as aliphatics, cycloaliphatics, gasoline, xylene, toluene; alcohols, such as ethanol, isopropanol, butanol, tert-butanol; ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, diethyl ketone, and ethers, e.g. tetrahydrofuran, diisopropyl ether, di-n-propyl ether, methyl tert-butyl ether, dioxane, and mixtures of the abovementioned solvents.

The temperature at which the substance B is applied is of relatively little importance for the success of the invention. The temperature selected will generally be one at which the substance B is liquid or has no remaining flow threshold. In other words, the substance B is generally applied at temperatures in the range  $T_1$  and above. The substance B can also be applied at temperatures markedly higher than  $T_1$ , for example at temperatures above  $T_1$  by at least 20 K, in particular by at least 30 K, and particularly preferably by at least 50 K, in order to reduce the viscosity of the substance B. However, the temperature of the substance may also be below  $T_1$  when it is applied to the surface, where appropriate with the aid of a solvent.

According to the invention, the amount of the substance B applied to the surface is sufficient for complete covering of the surface. Complete covering of the surface means an at least monomolecular layer of substance B. For complete covering, the degree of covering is at least 99% of the surface. Complete covering is generally achieved by applying at least  $10^{-3} \text{ g/m}^2$  of substance B, preferably at least  $5 \cdot 10^{-3} \text{ g/m}^2$ , in particular at least  $10^{-2} \text{ g/m}^2$ . The amount of substance B applied is in particular in the range from  $10^{-3} \text{ g/m}^2$  to  $100 \text{ g/m}^2$ , preferably in the range from  $5 \cdot 10^{-3} \text{ g/m}^2$  to  $80 \text{ g/m}^2$ , and in particular in the

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range from  $10^{-2}$  g/m<sup>2</sup> to 50 g/m<sup>2</sup>, particularly preferably from  $10^{-2}$  g/m<sup>2</sup> to 10 g/m<sup>2</sup>, and specifically from  $10^{-2}$  g/m<sup>2</sup> to 5 g/m<sup>2</sup>.

The surfaces thus obtained, and therefore also the articles or  
5 substrates which have this surface, are novel and are likewise  
provided by the invention. At a usage temperature  $T \geq T_1$ , liquids  
A have no, or only slight, adhesion to these surfaces, this  
paucity or absence of adhesion being expressed in terms of a  
contact angle hysteresis  $\Delta\theta = \theta_a - \theta_r$  of not more than  $40^\circ$ , in  
10 particular not more than  $20^\circ$ , and in particular not more than  $10^\circ$ .  
Even at small angles of inclination, the run-off of the liquids A  
from the surfaces of the invention is rapid, and there is  
therefore free movement on the surfaces. The result is no drying  
of the liquid droplets, so that no deposits form. Dirt particles  
15 are very easily and rapidly washed away from the surfaces by the  
liquids A. In addition, the optical properties of the untreated  
surfaces are retained.

The process of the invention is in particular suitable for  
20 producing surfaces which are not wetted, or are only slightly  
wetted, by alcohols, in particular polyols, such as glycerol and  
glycol, or by aqueous liquids, or to which these liquids do not  
adhere, or adhere only slightly. Aqueous liquids here and below  
are liquids which comprise at least 60% by volume, in particular  
25 at least 80% by volume, of water, based on the liquid  
constituents of the liquid. Other examples of aqueous liquids,  
besides water, are aqueous alkalis and acids, solutions in water  
of inorganic or organic materials, e.g. of salts, of sugars, of  
starch, of proteins, of surfactants, of alcohols, or of polymers,  
30 and also aqueous emulsions, dispersions, and suspensions.

The advantageous properties of the surfaces of the invention make  
them suitable for a wide variety of applications. For example,  
these surfaces can be used on articles exposed to severe soiling.  
35 This method not only reduces the soiling of the articles but also  
reduces corrosion resulting from soiling. The surfaces of the  
invention can also be used on the inner walls of tanks, the inner  
walls of storage containers for solids, the inner walls of  
pipelines and of chemical apparatus, and the like. The result is  
40 lower adhesion of liquids to the container walls. The  
self-cleaning action of the surface also reduces formation of  
deposits and permits easier removal of solid residues by  
cleaning.

45 The following non-limiting drawings and examples provide  
illustration of the invention.

## 16

Figure 1 is a diagram of an experimental arrangement for the coating of a substrate (1) with a liquid substance B, utilizing capillary forces. To this end, the substrate (1) is placed with one edge in a storage vessel (4) filled with the liquid substance B (3). Capillary forces here cause this substance B to migrate counter-gravitationally into the depressions of the substrate surface, thus forming a thin liquid film (2) on the surface of the substrate.

10 Figure 2 shows a scanning electron micrograph of the surface of a polyester film with a regular mountain-valley arrangement of elevations and depressions. The average distance between two depressions separated by any saddle area is about 2  $\mu\text{m}$ , and the average height difference between the elevations and depressions  
15 is about 10  $\mu\text{m}$ .

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## Examples

## I. Analysis

- 5 Determination of static, advancing, and receding contact angle, using a microscope equipped with a goniometer.

Determination of surface tension and surface tension at the boundary: pendant-drop method, e.g. as described by O. I. del  
10 Rio et al., J. of Colloid Interface Sci. 196 (1997), p. 136,  
J. P. Garandert et al., J. of Colloid Interface Sci. 1994,  
pp. 165, 351, K. Mysels, Colloid Surfaces 43 (1990), p. 241.

## 2. Preparation of coated substrates

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## Example 1:

Spherical particles of lycopodium (average particle size  
about 20  $\mu\text{m}$ ), commercially available from Fluka, were applied  
20 to an adhesive tape (TF) (Tesa Film, 1 x 1 cm, obtainable  
commercially from Beiersdorf), by scattering lycopodium on  
the adhesive tape and removing excess powder by blowing.

In an experimental arrangement as in Figure 1, the resultant  
25 substrate was immersed for 48 h with one edge (depth 1 mm) in  
a liquid polydimethylsiloxane (Rhodorsil 48V100, available  
commercially from Rhodia Chimie, viscosity  $\eta$  (20°C) = 102.5  
cSt). The polydimethylsiloxane here migrated  
counter-gravitationally into the depressions of the  
30 structure.

The static contact angle of water on the untreated surface of  
the substrate was 145°, and the static contact angle of the  
silicone oil on the untreated surface was < 10°. The surface  
35 tension  $\gamma_{\text{H}_2\text{O}}$  was 72 mN/m, and that of the polydimethylsiloxane  
 $\gamma_{\text{PS}}$  was 20.9 mN/m. The surface tension  $\gamma_{\text{H}_2\text{O}/\text{PS}}$  at the boundary  
was 30.1 mN/m (all values at 20°C).

The advancing contact angle  $\theta_a$  and the receding contact angle  
40  $\theta_r$  of water were determined for the substrate surface treated  
according to the invention, and for the untreated surface,  
for comparative purposes. The values found and the contact  
angle hysteresis calculated from these are given in Table 1.

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## Example 2:

Using a method similar to that of Example 1, the substrate shown in Figure 2 (available commercially as Truegrain MV from Autotype International Ltd., UK) was treated with a liquid, silanol-terminated polydimethylsiloxane (Silikon DMS-S12 from Gelest ABCR, viscosity  $\eta$  (20°C) = 26 cSt).

The static contact angle of water on the untreated surface of the substrate was 104°, and the static contact angle of the silicone oil on the untreated surface was < 10°. The surface tension  $\gamma_{H_2O}$  was 72 mN/m, and that of the polydimethylsiloxane  $\gamma_{PS}$  was 19 mN/m. The surface tension  $\gamma_{H_2O/PS}$  at the boundary was 27.7 mN/m (all values at 20°C).

The advancing contact angle  $\theta_a$  and the receding contact angle  $\theta_r$  of water were determined for the substrate surface treated according to the invention, and for the untreated surface, for comparative purposes. The values found and the contact angle hysteresis calculated from these are given in Table 1.

Table 1:

	Example 1		Example 2	
	untreated	treated	untreated	treated
$\theta_a$ H <sub>2</sub> O	145°	101°	104°	74°
$\theta_r$ H <sub>2</sub> O	0°	81°	0°	72.5°
$\Delta\theta$	145°	20°	104°	1.5°

## Examples 3 - 7:

Using a method similar to that of Example 2, a specimen of the substrate used in that example was treated with each of the following: decanol (viscosity  $\eta$  (20°C) = 12.4 cSt), 2-hexyldecan-1-ol (viscosity  $\eta$  (20°C) = 31.3 cSt), a polymethylhydrosiloxane (HMS 991 from Gelest ABCR, viscosity  $\eta$  (20°C) = 22.5 cSt), a silanol-terminated polydimethylsiloxane (Silikon DMS-S21 from Gelest ABCR, viscosity  $\eta$  (20°C) = 88.3 cSt), and a polydimethylsiloxane (Rhodorsil 48V100, available commercially from Rhodia Chimie, viscosity  $\eta$  (20°C) = 102.5 cSt). The static contact angle for these substances was in all cases < 10°. The results are given in Table 2.

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Table 2:

	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Substance B	Decanol	2-Hexyl-decanol	HMS 991 <sup>1)</sup>	S21 <sup>2)</sup>	48V100 <sup>3)</sup>
5 $\gamma_B$ [mN/m]	9.0	26.1	21.5	28.5	30.1
$\gamma_{H_2O/B}$ [mN/m]	28.8	27.1	19.7	20.4	20.9
$\theta_a$ H <sub>2</sub> O	54°	86°	89°	89°	90°
$\theta_r$ H <sub>2</sub> O	49°	83°	88°	89°	88°
10 $\Delta\theta$	5°	3°	1°	1	2°

1) polymethylhydrosiloxane

2) Silikon DMS-S21

3) Rhodorsil 48V100

### 15 III. Dirt removal test

20 A specimen from Example 1 was soiled by scattering with silica gel 60, from 0.04 to 0.063 mm (available commercially from Merck). Water was then applied dropwise to the specimen, which had been inclined at 20° from the horizontal. The water droplets run off the surfaces and thereby remove the dirt particles. The effectiveness of dirt removal was 95% increased in comparison with an untreated MV specimen without silicone oil. The droplets do not run off the reference specimen at an inclination angle of 20°.

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